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# RPI Rensselaer Polytechnic Institute

# Materials Research

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SEMI-ANNUAL PROGRESS REPORT

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Rensselaer Polytechnic Institute
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Semi-Annual Progress Report
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INTRODUCTION

During the summer of 1970 the Materials Research Center

staff members presented five courses which were directed toward the

industrial community.  Over 100 persons attended these sessions.  NASA

support of Rensselaer's materials research program was instrumental in

enabling Rensselaer to develop the areas of expertise and facilities

that made these courses possible, providing yet another example of

industrial spin-off from NASA sponsored programs.

The programs were "Principles of Color Technology"

coordinated by Dr. F. W. Billmeyer; "Color Technology for Management"

coordinated by Dr. F. W. Billmeyer: "Advanced Color Measurement"

coordinated by Dr. F. W. Billmeyer; "Electron Microscopy" coordinated

by Drs. G. S. Ansell and G. Judd; and "Sintering Technology" coordinated

by Dr. F. V. Lenel.

During the summer of 1970 Dr. A. C. Greene terminated his

association with the University.  A report of his studies on Electron

Spin Resonance is presented in the Structural Characterization section

of this report.  Research in some areas of Electron Spin Resonance will

continue under the direction of other staff members.

Also in the way of notable personnel changes, Dr. J. L. Katz

returned to the University after completing his year's leave of absence.

This nineteenth semi-annual report is again essentially a compendium of the reports on individual research projects divided into the four general areas of Structural Characterization, Solid State Reactions and Phase Transformations, Mechanical Properties and Strengthening Mechanisms, and Electronic and Physical Properties of Materials. Each area is preceded by a semi-technical introduction which gives a broad overview of the studies being pursued in that particular area.

STRUCTURAL CHARACTERIZATION

N71-19727

The current report on the structural characterization of materials has three areas of special interest: new directions, new facilities, and major progress in several continuing areas of research.

A new direction in our research on materials, evident for some time, now begins to take on major proportions. It is our interest in biological materials, specifically biopolymers. Programs are now underway to study the elastic properties of a variety of hard tissues and biomedical materials, and to relate them to structure at the molecular, supermolecular, and microscopic levels. The program includes both experimental and theoretical effort, and initial efforts are directed toward collagen; mineral and synthetic apatites; amorphous calcium phosphate from bone; such hard tissues as dentin, enamel, and related materials; and dental amalgams. In another research area related to biomaterials, equipment in the Polymer Characterization Laboratory is being prepared for a study of DNA from normal and neoplastic human tissue.

A major new facility, the Electron Microanalysis Laboratory, was established during this period as a result of increased use of the electron probe microanalyzer and the acquisition of a scanning electron microscope. The latter was used by no less than six research groups in the Materials Research Center during the first three months of its operation. The Polymer Characterization Laboratory has also acquired a versatile liquid chromatograph, capable of operation at

preparative as well as analytical levels, which is being used by several groups for the purification and separation of biological and synthetic organic materials.

Major progress is reported in several areas of continuing research. In studies of polymer-solvent interactions, the interfacial stress and deformation fields resulting from inhomogeneous swelling (by the admixture of solvent) of filled elastomers have been predicted accurately from theory. In the Polymer Characterization Laboratory, the refinement and new application of a summative fractionation technique has provided a method, as yet unequalled in accuracy, for determining the breadth of the molecular-weight distribution in narrow-distribution polymers. Structural and phase studies of inorganic materials have been extended during the period to elucidate the tempera-ture-composition phase diagram for the solid region of the system MnSe-CdSe in the temperature range 500 - 1100$^{o}$C.

# RELAXATION IN POLYMERS AT LOW TEMPERATURES

Senior Investigator:    R. K. MacCrone

The purpose of this research is to investigate the effect of excess vibrational modes, the presence of which are inferred from the specific heat measurement, on the mechanical and dielectric relaxations of amorphous polymers.

Dielectric and anelastic measurements have been made on polymethyl methacrylate and polystyrene at low temperatures. Anelastic measurement showed several distinct relaxations at low temperatures, while dielectric measurement showed broad peaks at around the same temperatures. Relaxation strengths were calculated assuming that the side groups of the chains in polymers are responsible for the relaxation phenomena as well as for the excess specific heat. Reasonable agreement was obtained between experimental observation and the theoretical prediction.

The results of this research were presented at the International Conference of "Physics of Non-Crystalline Solids" at Sheffield, England, and will be published in the Proceedings of the Conference.

POLYMER-SOLVENT INTERACTIONS

Senior Investigator:    S. S. Sternstein

## I.   Inhomogeneous Swelling in Filled Elastomers

The deformation and stress fields associated with the inhomogeneous swelling of an elastomeric matrix containing a spherical inclusion have been described in a previous report.  The anisotropic swelling gives rise to a birefringence field which can be used to verify the theoretical predictions.  Experiments have been performed on lightly cross-linked natural rubber containing glass spheres of 10 to 100 $\mu$m radius.  Typical results are shown in Figure 1, where the measured and theoretical retardations are shown as functions of reduced distance from the inclusion surface, for two swelling agents.

The excellent agreement with theory suggests that accurate prediction of interfacial stress and deformation in filled elastomers can now be obtained.  The interfacial radial stress produced by swelling has been calculated for various cross-link densities of the elastomer matrix and for various polymer-solvent interaction strengths, as measured by the Flory-Huggins parameter $(\chi)$, and is shown in Figure 2.  Similarly, the radial extension ratio of the elastomer immediately adjacent to the inter-face is shown in Figure 3.  Future work will involve the effect of particle-particle interactions and interfacial failure analysis using failure envelope techniques in conjection with Figures 2 and 3.

## II.   Constant Volume Polymer-Solvent Interactions

Data are now being obtained on various polymer-solvent systems.  Theoretical analysis of the constrained swelling problem requires accurate measurements of volume changes on mixing, and equipment is being designed to obtain such data.

NATURAL RUBBER
$\rho / M_c = 1.04 \times 10^{-4}$ mole/cc

——— theory
⊙ o-di-chlorobenzene
○ benzene

RETARDATION/R × $10^3$

(r/R)

FIGURE 1

FIGURE 2

RADIAL EXTENSION RATIO AT INTERFACE
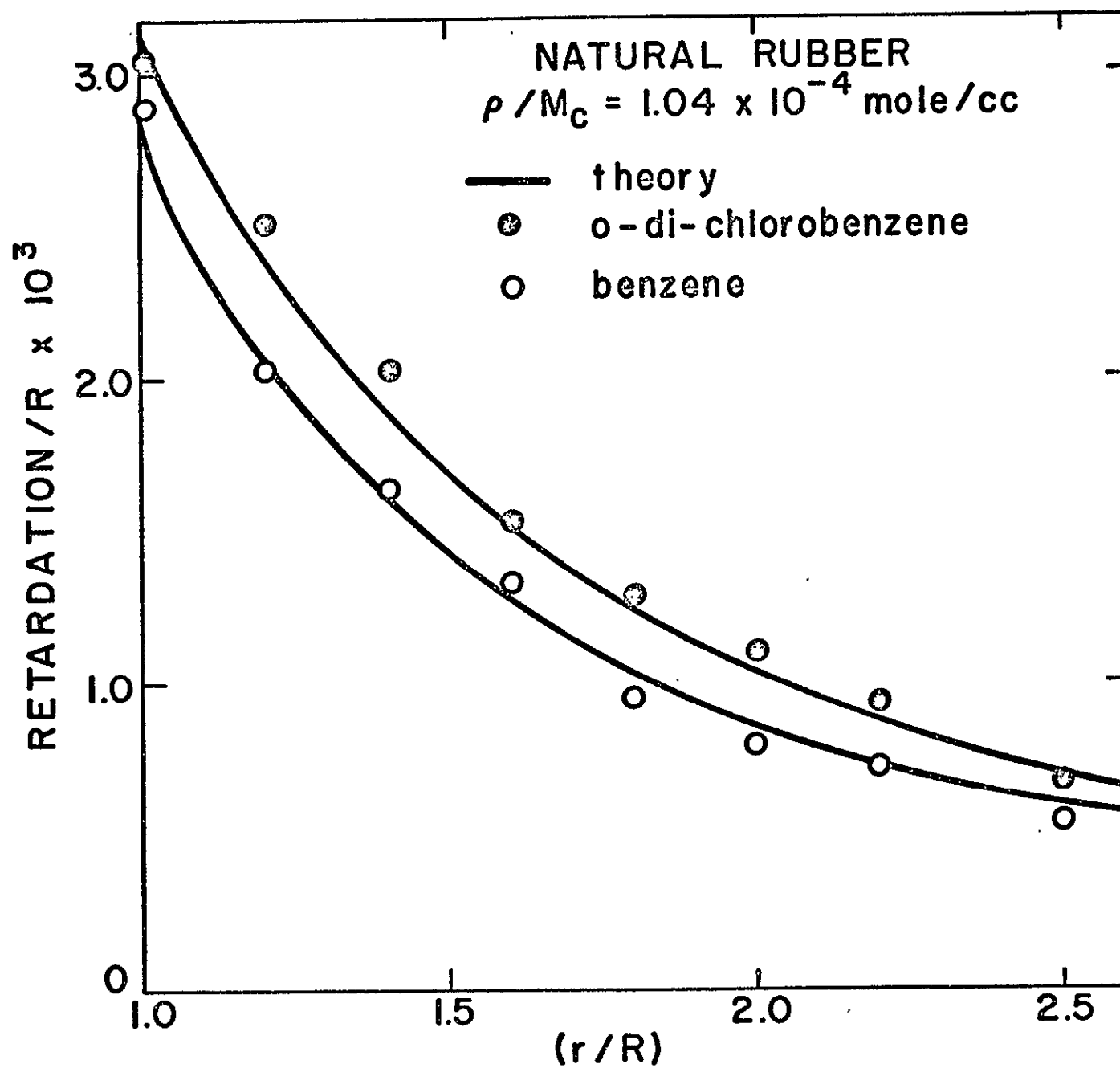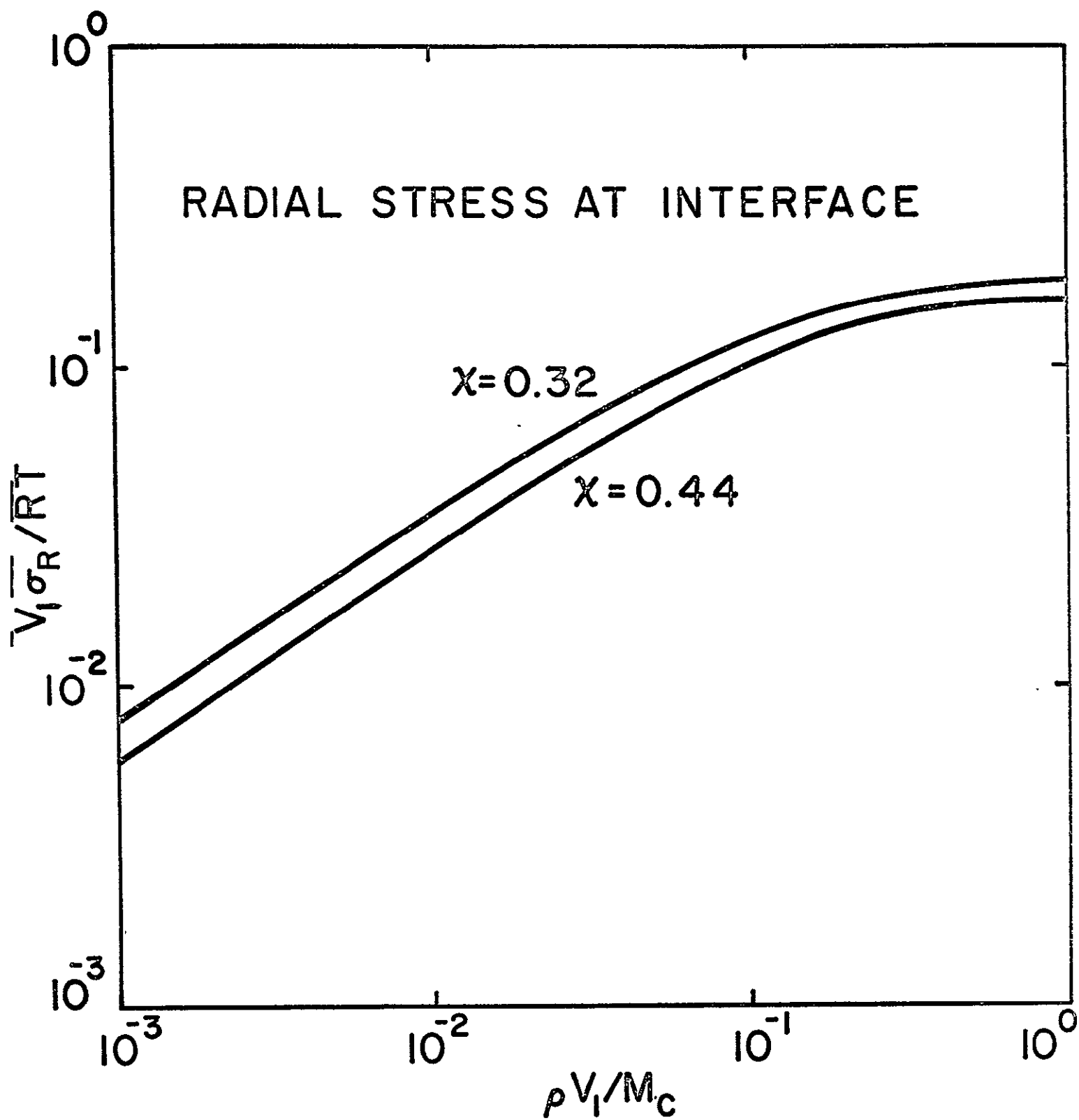
FIGURE 3
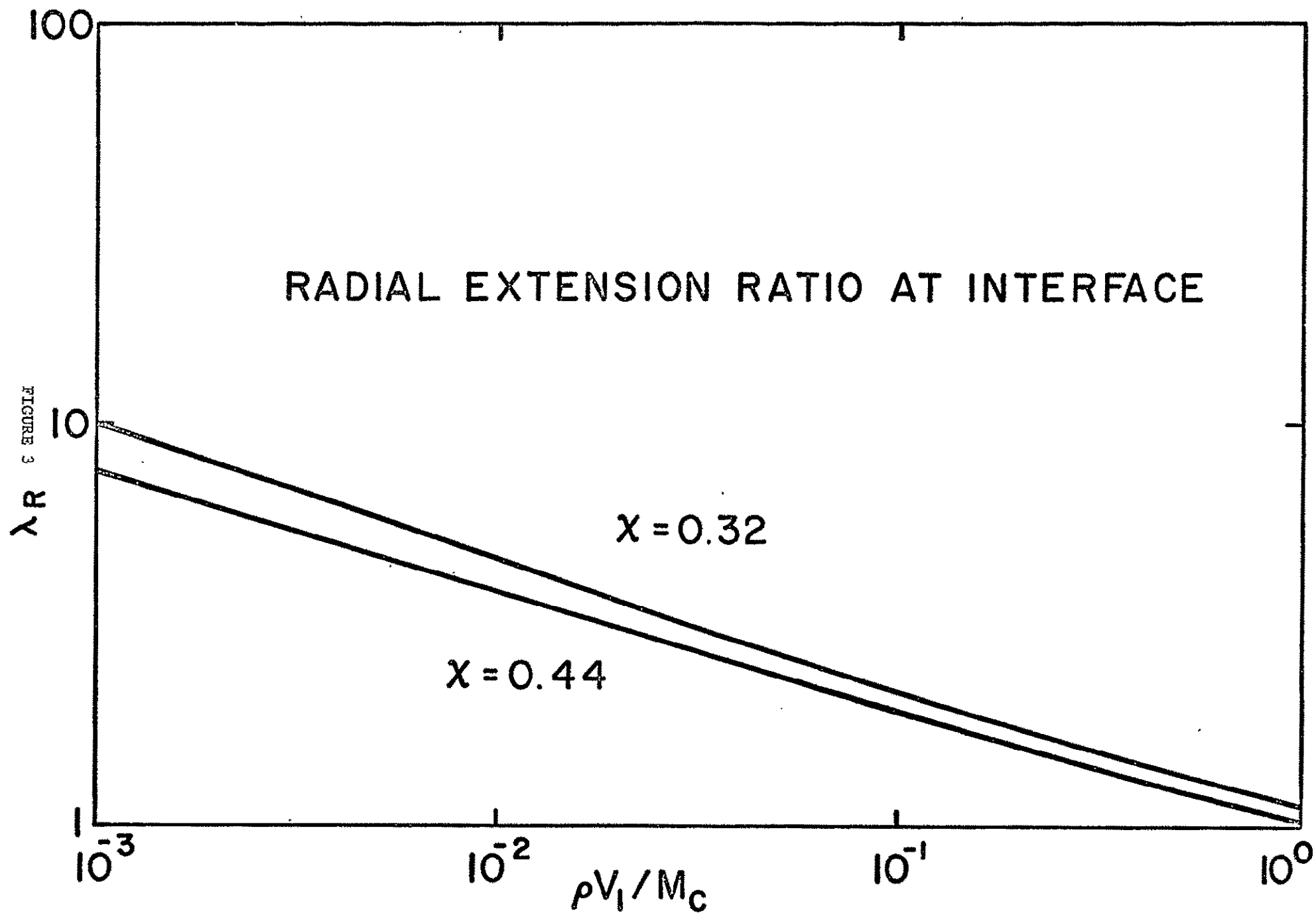
SOLUTION PROPERTIES OF POLYMERS

Senior Investigator:    S. Krause

## Properties of Vinyl Acetate Vinyl Alcohol Copolymers

Before studying the solution properties of these copolymers, we intend to investigate carefully the circumstances under which random and block copolymers are formed from vinyl acetate homopolymer and from vinyl alcohol homopolymer. We have continued our work with 2,4-pentanediol, the lowest molecular weight analog of these polymers.

The optical isomers of 2,4-pentanediol have been separated by means of ion exchange of their borate complexes. The meso-isomer is the lowest molecular weight analog of isotactic poly(vinyl alcohol) while the d and l isomers are analogs of syndiotactic poly(vinyl alcohol). Monoacetates and diacetates of these isomers have been prepared and purified. NMR spectra of all compounds have been obtained. We hope that the NMR spectra of these simple homopolymer and copolymer analogs will be useful in the interpretation of the NMR spectra of the high molecular weight copolymers that will be studied later.

## Mixtures of Block Copolymers with the Corresponding Homopolymers

A theoretical treatment of the conditions necessary for microphase separation in mixtures of block copolymers with one of the corresponding homopolymers has been developed as a function of block copolymer composition, molecular weight, number of blocks per molecule, interaction parameter between the corresponding homopolymers, and molecular weight of the added homopolymer. A paper entitled "Microphase Separation in Mixtures of Block Copolymers with the Corresponding Homopolymers: Zeroth Approximation" was presented as part of a Symposium on Colloidal and Morphological Behavior of Block and Graft Copolymers at the Fall, 1970 Meeting of the American Chemical Society in Chicago, Illinois.

## LOW-ANGLE LIGHT SCATTERING STUDIES

Senior Investigator:     F. W. Billmeyer, Jr.

Our low-angle light scattering photometer is being prepared to measure the molecular weights of various samples of DNA. The goal of the project is to measure and compare the molecular weights of samples of DNA taken from normal and neoplastic human tissue, in order to determine whether any real differences exist.

During this report period, several mechanical and optical modifications were made to facilitate the measurement of absolute scattering intensity. Slippage in the angle counter was eliminated by installation of a direct-drive assembly. Slits were added to the lamp-house aperture to eliminate stray light. The monochromatic filter assembly was modified to handle two high-quality interference filters interchangeably. A new field lens of highest optical quality was installed to improve beam resolution. Further optical modifications are anticipated in order to make the main slit width variable, and to alter the field slits and receiver slits so that complete angular scans will be possible. The size and shape of the scattering cell will also be changed to facilitate this type of operation.

A rigorous optical alignment of the instrument will be undertaken upon the completion of these modifications.

THERMODYNAMICS OF POLYMER SOLUTIONS

Senior Investigator:     F. W. Billmeyer, Jr.

Vapor-sorption studies of toluene into polybutene-1 in the range of $50^{\circ}$C to $65^{\circ}$C in five-degree increments are now complete. The results indicate that the three samples of polybutene-1 remain relatively inert to toluene at these lower temperatures.

To extend the experiments to higher temperatures, a new glass sorption apparatus has been constructed which is larger to allow the use of larger samples and longer spring extensions, and also incorporates a mercury U-tube which allows the measurement of pressures up to 45cm of mercury. This permits the investigation of the system toluene/polybutene-1 up to temperatures slightly in excess of $90^{\circ}$C. A new welded aluminum constant-temperature bath has also been constructed to hold the sorption cells. It allows a view of the entire apparatus through glass windows which are 20 inches in height.

Sorption runs at $60^{\circ}$C with the new apparatus have given data which agree well with previous results. A $70^{\circ}$C run is now in progress and will be followed by a run at $80^{\circ}$C and possibly one at $90^{\circ}$C, if it appears likely that the higher temperature will yield further useful information.

Also to be analyzed are three samples of polybutene-1 which have been subjected to boiling hexane in a Sohxlet extraction apparatus for times of 75, 150 and 300 hours respectively. Sohxlet extraction of $\alpha$-olefins using boiling diethyl ether is a well-established technique to remove amorphous material from crystalline samples. Since the solubility parameter of hexane is very similar to that of ether, while hexane is much less hazardous to use, this was the solvent of choice. DTA and DSC analyses of these samples are in progress.

## CHARACTERIZATION OF NARROW DISTRIBUTION POLYMERS

Senior Investigator:    F. W. Billmeyer, Jr.

The method of summative fractionation [Billmeyer and Stockmayer, J. Polymer Sci. $\underline{5}$, 121 (1950)] has been applied to narrow-distribution polymers with some success. Experiments were made with an anionic polystyrene with $\overline{M}_w/\overline{M}_n$ "less than 1.15" (probably around 1.05) and $\overline{M}_w$ = 97,600. Analysis of the data indicated that one should be able to determine $M_w/M_n$ within the following limits:

| Assumed $\overline{M}_w/\overline{M}_n$ | Upper and Lower 95% Confidence Limits on $\overline{M}_w/\overline{M}_n$ |
|---|---|
| 1.005 | 1.003 - 1.008 |
| 1.01 | 1.0065 - 1.015 |
| 1.02 | 1.014 - 1.027 |
| 1.05 | 1.038 - 1.065 |
| 1.1 | 1.078 - 1.13 |
| 1.2 | 1.16 - 1.25 |
| 1.5 | 1.4 - 1.7 |

For the higher values of $\overline{M}_w/\overline{M}_n$, these results agree in order of magnitude with those in the original article. For the lower values of $\overline{M}_w/\overline{M}_n$, no other method known to us approaches this level of absolute accuracy.

Unfortunately, the experimental work was terminated abruptly with the entry of the student into the armed forces. We expect to complete the determination of $\overline{M}_w/\overline{M}_n$ for the one sample being studied, at least, during the coming period.

Since the anionic polystyrenes conform to the Poisson distribution of molecular weights of the individual species, theoretical calculations were made of the major parameter of the summative-fractionation technique, H*, as a function of $\overline{M}_w/\overline{M}_n$ for both the Poisson distribution and several others studied in 1950, in the range $1.0 < \overline{M}_w/\overline{M}_n < 1.2$. In this region, we found that it makes very little difference which distribution function is used, confirming our prediction that the technique yields $\overline{M}_w/\overline{M}_n$ virtually independent of the details of the distribution, but conversely gives virtually no information about those details.

STRUCTURAL AND PHASE STUDIES OF INORGANIC MATERIALS

Senior Investigator:    H. Wiedemeier

The objectives of this program are investigations of phase equilibria and transformations in the solid region of inorganic systems and materials with technologically desirable properties. Recent developments indicate an increasing demand in alloy compounds for solid-state devices. This requires a precise knowledge of the structural properties of such materials.

As a continuation of previous studies, the temperature-composition phase diagram for the solid region of the system MnSe-CdSe has been established in the temperature range $500^{\circ}$-$1100^{\circ}$C. Debye-Scherrer x-ray diffraction techniques were used to identify the phases in equilibrium. The degree of solid solution was determined from the change in lattice parameter as a function of composition and from the onset of the second phase. Lattice parameters for compositions with cubic structure were obtained from high-angle reflections by the extrapolation method. Lattice constants for compositions in the hexagonal region were calculated by the reciprocal-lattice method.

The phase diagram shows a cubic (NaCl structure) one-phase region between 0 and about 10 mole % CdSe and a hexagonal (wurtzite structure) one-phase region between 50 and 100 mole % CdSe, separated by a two-phase region. The phase boundary of the cubic phase is strongly temperature dependent, whereas the hexagonal boundary is practically temperature independent. The small degree of solid solution on the MnSe-rich side compared to the wide CdSe-rich one-phase region can be explained by the differences in structural and bonding properties of

the components. MnSe exists in the stable NaCl-type structure and in the metastable zinc blende and wurtzite structures. The stable modification of CdSe at room pressure is the wurtzite structure. Based on this, one would expect that MnSe can easily be accommodated in the CdSe host lattice, since it requires only a rearrangement of the MnSe structure to a metastable modification with a change in bonding from octahedral to tetrahedral configuration. The electronic structure of manganese permits both configurations, with s-p-d and s-p orbitals, respectively. In order for cadmium to form octahedral bonds in the NaCl structure, higher d orbitals have to be used; this is energetically unfavorable. This type structure can only be obtained for CdSe through the application of high pressure. These bonding properties explain the existence of only the wurtzite modification of CdSe at room pressure and the narrow range of solid solubility of CdSe in MnSe.

It was observed in these studies that the individual lattice parameters change linearly with composition within narrow limits of experimental error. The change in lattice constants of the one-phase compositions can be expressed for the MnSe-rich cubic phase by the equation

$$a_o = 5.462 + 0.202 \ N, \tag{1}$$

and for the CdSe-rich hexagonal phase by the equations

$$a_o = 4.173 + 0.124 \ N \tag{2}$$

and

$$c_o = 6.822 + 0.193 \ N, \tag{3}$$

where N is the mole fraction of CdSe and $a_o$ and $c_o$ are in $\overset{o}{A}$-units.

Assuming that Vegard's rule holds for a complete substitution of $Mn^{2+}$ for $Cd^{2+}$ in the hexagonal phase, equations (2) and (3) yield lattice parameters for MnSe in the wurtzite structure, namely $a_o = 4.173$ Å and $c_o = 6.822$ Å, in general agreement with older literature data[1] ($a_o = 4.12$ Å, $c_o = 6.72$ Å). It should be mentioned that it is difficult to obtain reliable lattice parameters from direct measurements on metastable substances. A similar evaluation of equation (1) yields a lattice parameter for CdSe in the NaCl structure, $a_o = 5.664$ Å. Mariano and Warekois[2] studied the high-pressure transformation of CdSe from the wurtzite to the NaCl-type modification and obtained a value of 5.49 Å for $a_o$ at a pressure of 32 kbar. Rooymans[3] found a value of 5.54 Å for the lattice constant of CdSe with NaCl structure at a pressure of 30 kbar. The trend in these values could suggest that, in addition to the rearrangement of atoms to form a structure of higher coordination, the interatomic distances are reduced due to the applied pressure. The value derived from solid-solution studies in our laboratory by a Vegard-law extrapolation is based on ideal substitution at room pressure, which does not consider possible compressibilities of the atoms at high pressures. This technique offers a convenient method to compute lattice parameters for pure metastable phases which are otherwise difficult to obtain.

These studies are being extended to the manganese-cadmium-tellurium system with increasing differences in structural properties.

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[1] R. W. G. Wyckoff, "Crystal Structures," Vol. I, Chap. III, Table III, 11, p. 31, Interscience Publishers, Inc., New York, 1948.

[2] A. N. Mariano and E. P. Warekois, Science, 142, 672, 1963.

[3] C. J. M. Rooymans, Phys. Rev. Letters, 4, 186, 1963.

## IMPURITY DIFFUSION RATES

Senior Investigator:    H. M. Gilder

Turnbull and coworkers have suggested that the diffusion of the noble metals, silver, copper and gold, in the lead lattice is dominated by an interstitial mechanism. Although the interstitial solution of these metals is strictly forbidden by the classical metallurgical size rules governing solid-solid solution, d-d shell dispersion binding of the impurity and host isoelectronic ion cores can apparently lead to an interstitial solubility of ~1% (the remaining ~99% of the impurities dissolve substitutionally). This is enough, however, to have the substitutional impurity - lead vacancy exchange dominated by the motion of the interstitial impurity, since $D_{interstitial} >>> D_{subst.-vac.}$ (D = diffusion coefficient). To provide direct evidence of the existence of this interstitial mechanism we are presently engaged in studying the effect of high pressure (0 - 10 kbar) on the diffusion of silver in lead. Pressure can be used to detect the crystal volume change accompanying the diffusional jump of the impurity atom. We would expect a small volume change (relative to an atomic volume) for the interstitial jump, since the usual rather large change of crystal volume associated with the formation of a vacancy obviously does not enter.

## THERMAL EXPANSION MEASUREMENTS OF VACANCY FORMATION PARAMETERS

Senior Investigator:    H. M. Gilder

The purpose of this research is to measure the thermal equilibrium concentration of point defects (such as vacancies) in zinc, as well as the kinetics of their formation. The most direct method of studying such effects involves a comparison of the fractional change in each lattice parameter, $\Delta a/a_o$, with the corresponding macroscopic fractional length change, $\Delta L/L_o$. The difference between these two quantities is a measure of the fractional increase in the number of atomic planes (due to the climb of dislocations) in the direction perpendicular to that of length measurement. According to recent precision x-ray measurements of the c-axis lattice parameter expansion in zinc, the present data for $(\Delta a/a_o)_c$ coincide with the previous data of Gilder and Wallmark for $(\Delta L/L_o)_c$ over the entire temperature range $19.5^o$ - $414.0^oC$. Thus, there is no systematic divergence of the two sets of data with increasing temperature, so that to within the precision of the measurements there is negligible climb of dislocations parallel to the basal plane. We are presently making measurements of the a-axis lattice spacing (the a-axis is in a direction perpendicular to the c-axis) to allow a comparison with the previous data for $(\Delta L/L_o)_a$. Presumably we will find the quantity $(\Delta L/L_o)_a$ - $(\Delta a/a_o)_a$ large enough to allow a reasonably precise determination of the number of vacancies present at high temperatures.

# QUANTITATIVE ELECTRON MICROPROBE MICROANALYSIS TECHNIQUES

Senior Investigator:     G. Judd

The efforts in this project have been divided into the following areas:  the establishment of the new Electron Microanalysis Laboratory which houses the electron probe microanalyzer and the newly-acquired scanning electron microscope, the development of a technique to measure the amount of material transferred in an electrical contact, and the continued work on the application of computer programs to quantitative electron probe microanalysis.

The Electron Microanalysis Laboratory was established as a result of increased use of the microprobe and the purchase of a scanning electron microscope.  The scanning microscope now provides a new electron optics capability for surface and topography research carried out in the Materials Research Center and is already being used by six research groups in the Center even though it was only installed in June 1970.  In addition, the Microanalysis Laboratory has acquired an energy dispersive x-ray spectrometer which is being used in conjunction with the microprobe.

The study on material transfer upon contact of two metals requires the ability to measure extremely small amounts of material ($10^{-12}$ grams) irregularly distributed over a circular area (approximately 100 $\mu$m radius).  This type of measurement is extremely difficult by conventional microradiographic techniques.  Electron probe microanalysis was selected as a possible solution to this measurement problem.  The technique developed utilizes both the x-ray microanalysis and the scanning features of the microprobe in such a way that an area of interest can be examined and compared with prepared standards.  The sensitivity and reproducibility of this technique are good.  Measurement of as little as $3 \times 10^{-12}$ grams of lead transferred onto a gold substrate has been made.

# NUCLEAR MAGNETIC RESONANCE

Senior Investigator:     P. A. Casabella

The study of the quadrupolar polarization of ions in solid alkali halides under uniaxial strain now seems to be complete. Satisfactory agreement between experiment and theory has been obtained by considering the effects of overlap between nearest and next nearest neighbors, and of ionic contraction in the solid. It was assumed that the free ion electron wave functions contract uniformly when put in the solid. This was handled by replacing the wave function $\Psi(r)$ by $\Psi(\alpha r)$ where $\alpha$ is greater than one.

The contraction factor, $\alpha$, was determined by comparing the calculated and experimental values of magnetic susceptibility for the crystal under study. The value thus selected was then used to calculate the quadrupolar polarizability and the interionic repulsive energy parameter. Agreement between theory and experiment was greatly improved in both cases. The contraction factors used for NaCl, NaBr, KCl, and KBr are tabulated below.

| Ion | $\alpha$ |
|-----|----------|
| $Cl^-$ | 1.132 |
| $Br^-$ | 1.111 |
| $K^+$ | 1.023 |
| $Na^+$ | 1.000 |

## ELECTRON SPIN RESONANCE

Senior Investigator:     A. C. Greene

Various studies of radiation damage and annealing in undoped alkali halides by nuclear magnetic resonance, electron spin resonance, optical absorption, and volumetric expansion have suggested that stable interstitial molecular halogen complexes which complement the F center may be formed. The simplest molecular complex is the interstitial halogen molecule. In the present work, the energetics and strain fields associated with interstitial $Cl_2$ in NaCl and KCl have been studied by formulating the energy of the lattice plus molecule in terms of the coordinates of the lattice ions and the molecule, and then minimizing this energy relative to these coordinates. For these calculations, a general lattice energy minimization technique free from artificial constraints on ion relaxation has been developed and used with a Born-Mayer type of lattice potential corrected for the polarization of the lattice ions. The interaction between the lattice and the molecule has been characterized by repulsive energy parameters computed from Hartree-Fock-Slater wavefunctions with the aid of a phenomenological model. The calculations indicate that the energy of the interstitial $Cl_2$ relative to the perfect lattice is about 3.4 eV in NaCl and 1.6 eV in KCl. In both lattices the molecule was found to be compressed slightly (<1%) relative to the free state. Supplementary calculations of the energetics of H centers in NaCl and KCl have suggested that the binding energy of the interstitial chlorine molecule relative to two isolated H centers is about 3.6 eV in KCl and about 0.6 eV in NaCl.

STUDIES OF THE PHYSICAL PROPERTIES OF HARD TISSUES AND BIOMEDICAL MATERIALS

Senior Investigator:    J. L. Katz

Experimental and theoretical studies in the areas of biomedical materials and the biomechanics of hard and connective tissues can be categorized as follows:

## Elasticity of Collagen (Experimental)

Studies of the elastic properties of collagen in rat-tail tendon are in progress using equipment which has been modified and adapted for this purpose. Creep and stress-relaxation measurements are also available with this system. Optical studies of the collagen, using polarized light, are performed simultaneously in order to study the alignment of microscopic fibril elements within the fiber bundle as a function of stress.

Instrumentation of a similar apparatus for combined use with both wide and small angle x-ray scattering is in process. This will be used to study the behavior of collagen on both the molecular and ultrastructural level while it is undergoing stress.

## Elasticity of Collagen (Theoretical)

In progress are calculations of the elastic properties of collagen. This involves modeling on the molecular level as well as including fibril-fibril interactions in order to obtain elastic stiffness coefficients for collagen.

## Elastic Properties of Apatites (Experimental)

Ultrasonic studies of the elastic properties of mineral and synthetic apatites have been continued. Values of bulk and shear

moduli measured this way in polycrystalline aggregates of fluorapatite agree very well with the moduli computed from elastic stiffness coefficients recently measured in single crystals by other workers.

## Elastic Properties of Apatites (Theoretical)

The experimental values obtained in the above program have been used as the basis for calculations aimed at assessing the anisotropic properties of hydroxyapatite and its contribution to the anisotropic properties of calcified tissues.

## Properties of Amorphous Calcium Phosphate (ACP)

The role of ACP in bone growth dynamics is an important area of research. The conversion of ACP to crystalline hydroxyapatite has been studied by laser, light, and x-ray scattering techniques, spectrophotometry, and ion-electrode measurements. A model for explaining calcification of biological tissues based on ACP-induced heterogeneous nucleation of hydroxyapatite is under examination.

Small and wide angle x-ray scattering studies are also being used in an attempt to derive the molecular configuration of ACP; computer methods are used to calculate radial distributions and pair correlation functions from the x-ray data.

## Elastic Properties of Hard Tissues (Experimental)

The major effort in these studies has been concerned with experimental measurements of the elastic properties of hard tissues of various types (dentin, enamel, femur, tusk, mandible, vertebrae, etc.) from different species (human, fish, bovine, elephant, whale, etc.). X-ray diffraction, electron microscopy and diffraction, electron microprobe, scanning electron microscopy, and light microscopy are being used to

categorize the composition and structure as well as the degree of porosity and anisotropy of the materials studied in order to relate observed function and behavior and measured properties to molecular, ultrastructural, and microscopic levels of organization of the various calcified tissues.

A hydrostatic pressure cell capable of attaining pressures up to 10 kbar is being built for pressure-dependent studies of the physical properties of intact specimens of hard tissues as well as of biomaterials in a fluid medium. Of special interest here is the behavior of these systems in the 1 kbar region of pressure. Initial measurements will be concerned with the effects of porosity and liquid environment on the elastic behavior as measured by ultrasonic techniques.

Elastic Properties of Hard Tissues (Theoretical)

Concurrent with the experimental program on the elasticity of hard tissues is an intensive theoretical program analyzing the behavior of these tissues as multiphase composite materials. Various analytical composite models have been introduced in order to obtain approximate bounds on the elastic properties of hard tissues on an ultrastructural level involving only the two major phases, collagen and hydroxyapatite. The effects of the amorphous ground substance, basically mucopolysaccharides, and the amorphous calcium phosphate mineral present in many hard tissues has not as yet been directly included in these calculations.

Additional calculations are aimed at understanding the composite behavior at the microscopic level of organization, i.e., osteones and interstitial lamellae embedded in a low modulus viscoelastic matrix (known as the cement line and believed to be comprised of the same ground substance mentioned above). In this case, fiber-reinforced composite

micromechanics is being utilized. The complexity of these model-type calculations has required extensive use of computer facilities.

Physical Properties of Biomedical Materials

The study of the $\gamma_2$ ($HgSn_{7-8}$) phase of dental amalgam is being continued. The prime motivation is to understand the mechanism of the $\gamma_2$ phase disappearance previously noted and reported. The effects of pressure and metallurgical treatment are being studied by x-ray and electron beam techniques.

Ultrasonic measurements of the elastic properties of various porous ceramic and metallic systems have been initiated. Porous ceramics and metals are presently under extensive study at other laboratories as bone implant materials because of the possibility of dynamic stabilization by the ingrowth of calcified tissue through the interconnecting pores of the prosthetic or restorative device. In addition, there is the possibility of obtaining a closer match between the elastic and mechanical properties of the host and implant materials. Presently being studied for comparison with similar measurements on hard tissues are the elastic properties of samples of calcium aluminate, Co-Cr base alloys, Ti, and Ti-6Al-4V at various levels of porosity.

NOTE

Theoretical studies on x-ray thermal diffuse scattering are being continued at a reduced level of effort.

## LASER FUSION BONDING OF CERAMIC MATERIALS

Senior Investigator:      R. J. Diefendorf

This research project utilizes the laser as a tool with which glasses, ceramics, and other multiphase materials can be joined by fusion. High-melting materials such as fused silica have been effectively "welded" to produce shapes never before achieved except by very difficult procedures (e.g., in "Vycor" glass).

A $CO_2$ laser was chosen for the research because it has the necessary power density and was readily available. Another advantage of the $CO_2$ laser is its wavelength, 10.6 microns: many ceramic materials are highly absorbing in this region, and therefore, surface fusion occurs relatively readily.

We have studied subsurface changes in the morphology of human teeth due to surface fusion. Hydroxyapatite, dental hard tissue, is highly absorbing at the $CO_2$-laser wavelength, as Figure 4 shows. Laser-beam exposure of a dental enamel surface produces the glass-like fusion seen in Figure 5. Further studies of sectioned teeth after laser impingement on enamel surfaces shows that there is a definite penetration or diffusion of the fused material along the crystallites of hydroxyapatite. This provides evidence that bonding can take place via fusion. Penetration and subsequent solidification of the fused mass permanently seals the pathways into the tooth, preventing the entry of oral micro-organisms which might eventually cause incipient carious lesions (tooth decay).

While channel pores similar to those in teeth do not exist in high-temperature firebrick, this material does exhibit the same glass-like fusion. The bond between the fused material and the brick is both chemical and physical and exceedingly strong.

It is expected that fusion welding of ceramics may be another valuable application of the laser.

FIGURE 4

CM⁻¹

Top axis: 1300, 1000, 800, 600, CM⁻¹ 500, 400

Left axis (ABSORBANCE): 0.0, .10, .20, .30, .40, .50, .60, .70, 1.0, ∞

Right axis (TRANSMITTANCE VERSUS WAVELENGTH OF HYDROXYAPATITE): 0.0, .10, .20, .30, .40, .50, .60, .70, 1.0, ∞

Bottom axis (WAVELENGTH (MICRONS)): 8.0, [10.0], 12.0, 14.0, 16.0, 18.0, 20.0, 22.0, 24.0

COMMON CO₂ LASER

✓ - found in CaHPO₄
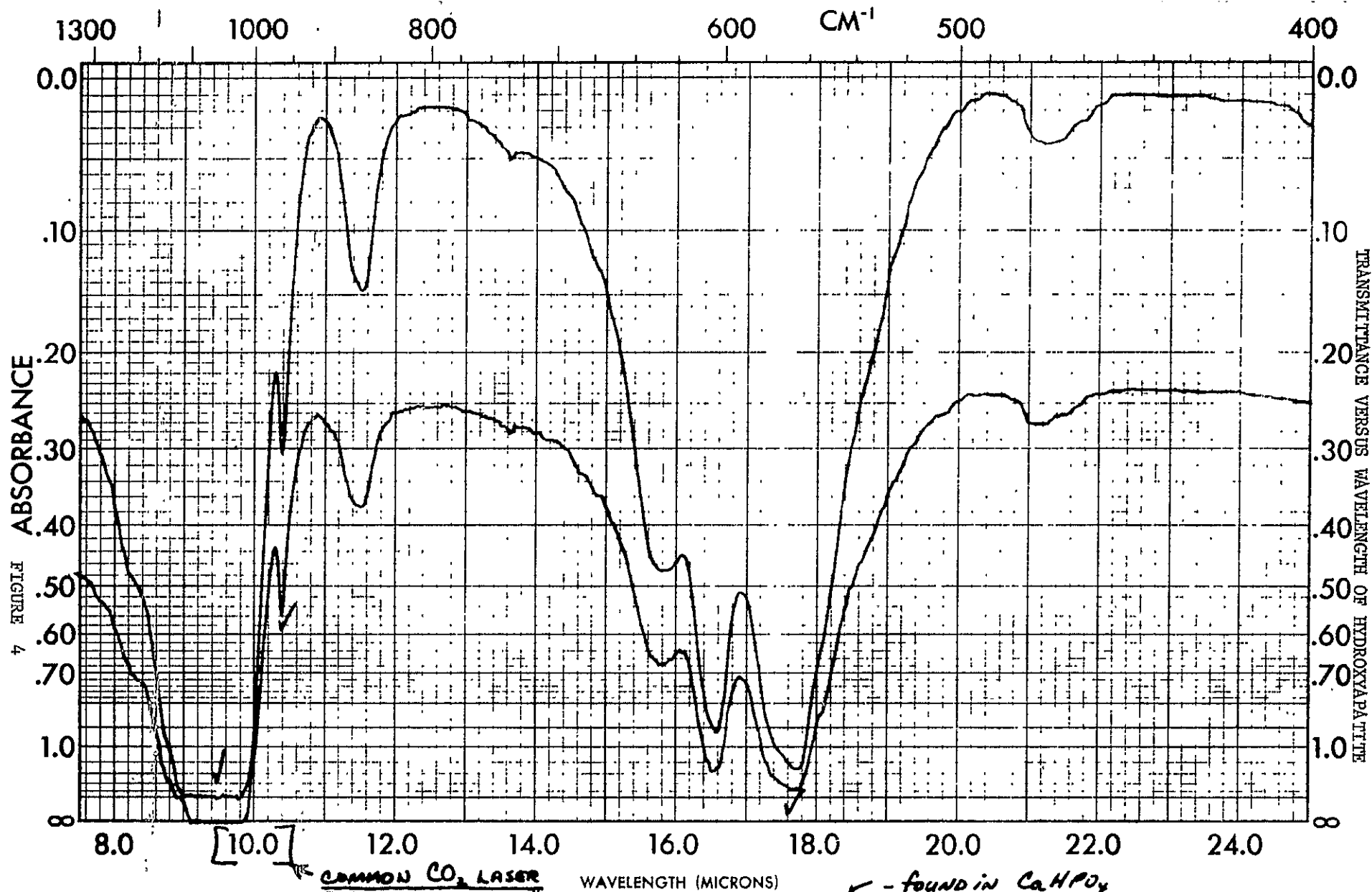
| SAMPLE 200 Mg KBr 2.5 mg HA | CURVE NO. | SCAN SPEED FAST | OPERATOR J.W. |
| | CONC. 1.25 % | SLIT N | DATE 3/4/65 |
| ORIGIN SYNTHETIC | CELL PATH | REMARKS UPPER ATTENUATED | |
| SOLVENT KBr | REFERENCE NONE | | |

PART NO. 337-1210

PERKIN-ELMER ®
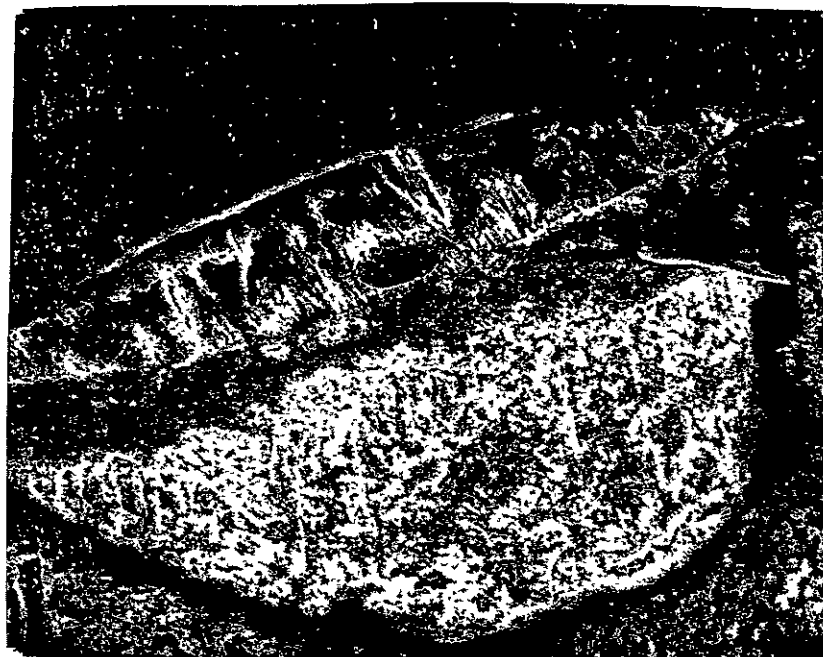
RESULT OF LASER IMPINGEMENT ON HUMAN DENTAL ENAMEL

FIGURE 5

SOLID STATE REACTIONS AND PHASE TRANSFORMATIONS

N71-19728

A principal objective in the study of solid materials is the use of solid state reactions and phase transformations to alter the structure of solids in order to attain specific structures and hence properties. On this basis, the foundation of solids research, the coupling of structure to property relationships, becomes a definitive reality. The research reported in this section is directed towards this goal; the understanding and utilization of basic transformations for a broad grouping of solid materials, with specific interrelationships to the overall view of materials research outlined in the other report areas. While the activities in this program area are given in detail following this introductory section, the highlights of the research results during this past program period are as follows:

Several studies have been directed towards achieving an understanding of the factors controlling the kinetics of solid state phase transformations. One which may have a significant practical application is the martensite transformation in steels, used to produce a wide range of high-strength alloys. Here very rapid quench rates have been used as a tool towards understanding the transformation kinetics and resultant strength for these alloys. From studies of the temperature dependence of the $Na^{25}$ nuclear quadrupole constant in Rochelle salt, it appears that a previously accepted model for ferroelectricity in this material is in doubt. The temperature dependence of the coupling constant was found to be much greater than had been previously assumed. Studies of the formation of precipitate free zones at grain boundaries in precipitation hardened aluminum alloys has continued. Electron microprobe analysis is

being utilized to investigate composition variations at grain boundaries as a function of minor alloy additions and heat treatment. The interest in this program has been directed towards correlation of the boundary structure of these alloys to their corrosion and mechanical behavior. Work is now starting using similar analysis techniques, to study pit corrosion in stainless steels.

Other programs in this area have centered on vapor-solid phase reactions. High temperature equilibrium vaporization studies have been pursued in order to determine the stability of the condenses phase and the thermodynamic properties. Here the interest is to provide the requisite information necessary for the reproducible synthesis of materials with desirable electro-optical properties. During this period, studies have centered on the mode of vaporization of cadmium selenide. In the polymer area, studies have centered on the crystallization of polymers from the gaseous phase in order to produce extended chain rather than folded chain crystals. Work on the simultaneous polymerization and crystallization of polyparaxylylene, however, formed crystal structures which seem not to be of extended chain nature. In contrast, polymeta-phosphates show extended chain crystals with high molecular weight without any chain folding.

# ELECTRON BEAM INTERACTIONS DURING THE OXIDATION OF THIN ALUMINUM FOILS

Senior Investigator:      G. S. Ansell

Previous work in this laboratory had shown that as thin aluminum foils were heated in the hot stage of an electron microscope, not only did aluminum oxide form, but also following oxidation aluminum was observed to subsequently precipitate within the oxide. In order to determine the nature of this rather unexpected event, a study of the formation of this precipitate phase has been undertaken. In this program, the oxidation of thin aluminum foils has been studied in situ, in the hot stage of the electron microscope, over the pressure range of $10^{-6}$ torr to $10^{-3}$ torr. Studies to date have demonstrated that the precipitation of aluminum within the oxide is the result of electron capture within the oxide during oxidation. These charge centers attract aluminum ions that are diffusing through the oxide. When they meet a recombination process occurs forming aluminum nuclei. These nuclei in turn continue to charge from the beam, being surrounded by an insulator, the charge is maintained and continued precipitate growth occurs by further attraction of diffusing aluminum ions. Further studies of the formation and growth kinetics of this process are continuing.

MARTENSITE TRANSFORMATION

Senior Investigator:     G. S. Ansell

This program is part of a continuing study of the kinetics and resultant strength characteristics of the martensite transformation in the Fe-C system.

Several approaches are being used in this study.  In the first, studies of the effect of solute elements which change carbon diffusivity in austenite upon the nature of athermal stabilization during rapid quenching has been continued.  We had previously established that such rapid quenching increases dramatically, as much as $200^{\circ}$F, the $M_s$ temperature of a series of alloy steels.  The purpose of this aspect of the program was to determine the role of solute elements upon this aspect of the transformation kinetics.  Here, we are investigating the effect of quench rate upon the $M_s$ temperature of Fe-C-X alloys in which the nominal $M_s$ temperatures of these alloys are similar while the effect of the X element on carbon diffusivity is quite variable.  The results of this study indicate that the quench rate effect of the $M_s$ temperature is directly related to the rate of carbon diffusivity in the austenite as predicted by the strengthening model we had previously proposed.  It was found that the $M_s$ temperature in these ternary alloys varied with temperature in a sigmoidal fashion.  The $M_s$ temperature first remaining constant until some minimum threshold quench rate is reached, increasing with increased quench rates above this threshold, and then leveling off to a maximum value of $M_s$ temperature when the quench rate exceeded a saturation value.  The threshold and saturation quench rates increased with increased rate of carbon diffusivity in the austenite.

The second approach has been to relate the entire transformation kinetics to the flow stress characteristics of the austenite. Here it was shown that the $M_s$ temperature varied, as predicted previously, with the austenite yield strength, decreasing with increasing yield strength. The extent of transformation as a function of cooling below the $M_s$ temperature was found to vary with the energy required to allow the plastic deformation associated with the volume change accompanying the austenite to martensite transformation. The extent of transformation per degree of undercooling was observed to increase with an increase in the produce of the austenite work hardening rate and the volume strain accompanying the transformation.

The third approach has been to consider the effects of fast quench rates on the strength of as-quenched martensite. Previously, we have shown that the hardness of as-quenched martensite decreases as the quench rate during the austenite to martensite transformation is increased. During this program period, the as-quenched hardness has been determined as a function of quench rate for the same series of Fe-C-X alloys which were described previously in the $M_s$ studies. It was found that the hardness varied sigmoidally with quench rate in a similar manner as did the $M_s$ temperatures for these alloys, the threshold and saturation quench rates for the hardness variation paralleling the $M_s$ behavior. Thus, these data tend to link quench rate effect on strength to the rate of carbon diffusion in austenite. Tempering, however, appears to recover this hardness decrease. During this year, a study has been started to determine the effect of subsequent tempering on the strength of these rapidly quenched steels. Here the hardness of fast quenched steels has been measured as a function of tempering time at room temperature and

alloy content. The data thus far obtained indicates that the hardness of these alloys increases upon tempering, reaching the as-quenched hardness obtained at normal quench rates. Transmission microscopy studies of the structure of these alloys, however, indicate that although the hardnesses of the fast quenched and tempered steels are the same as the normally quenched steels, their structures are quite different. There are no resolvable carbides present in the former while carbides are present in the normally quenched steels.

# THERMODYNAMIC AND KINETIC STUDIES OF SOLID-GAS PHASE REACTIONS AT HIGH TEMPERATURES

Senior Investigator:    H. Wiedemeier

The objectives of this work are the determination of thermodynamic and kinetic properties of solid phase-gas phase reactions. These investigations provide useful information for the synthesis of materials with desirable electro-optical properties. It is well known that the performance of such materials is critically dependent on composition and possible changes in stoichiometry at elevated temperatures.

It was established in previous studies that the stoichiometry of cadmium selenide changes slightly upon heating CdSe under vacuum at temperatures around $450^{\circ}C$. Under these conditions a preferential vaporization of selenium is observed causing the composition of the solid phase to shift to $CdSe_{1-x}$. Mass analysis of sublimed material and residue in connection with x-ray diffraction studies showed that the stoichiometry of CdSe changes less than 0.2 mole %, i.e., $X < 0.002$. After this steady-state condition is reached the non-stoichiometric compound vaporizes congruently at elevated temperatures according to the reaction

$$CdSe_{1-x}(s) = Cd(g) + \tfrac{1}{2}(1-x) Se_2(g).$$
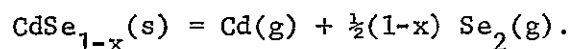
Although the deviation from stoichiometry is small, failure to consider the preferential loss of selenium during the initial heating period can lead to incorrect vapor pressures particularly in static measurements.

Based on the above steady-state reaction Knudsen type vaporization studies using quartz effusion cells and an automatic semi-micro vacuum balance were carried out in the temperature range $600^{\circ}-800^{\circ}C$.

Because of insufficient thermochemical data on this system, it was neces-
sary to determine the heat capacity of CdSe at higher temperatures in
order to evaluate the vapor pressure data in terms of standard thermodynamic
quantities.

The heat capacity measurements were performed in the DSC
cell attachment of a DuPont 900 Thermal Analyzer. For this purpose, a
300 mg sample of CdSe, prepared by direct sublimation of high purity
elements followed by vacuum annealing to attain the steady-state condition,
was pressed into a pellet at a pressure of 13 kbar. A packing density
of about 0.96 was achieved. The compressed sample was hermetically
sealed in an aluminum capsule to reduce the free volume to a minimum.
High purity alumina was used as a reference material. During the runs
the DSC cell was purged with dry nitrogen (99.99% purity). Measurements
were recorded at $5^{\circ}$ intervals between $50^{\circ}$ and $490^{\circ}$C for three separate
runs yielding a total of 264 data points which were averaged and reduced
to 88 points. A plot of $C_p$-values versus temperature showed that the heat
capacity of CdSe increases linearly in the applied temperature range.
This behavior justified application of a linear least squares analysis
of the data to express the change in heat capacity with temperature in
form of a two-term expansion. The derived heat capacity function of CdSe
is

$$C_p^{\,o} = 12.36 + 1.45 \cdot 10^{-3}T \ (\text{cal} \cdot \text{deg.}^{-1} \cdot \text{mole}^{-1})$$

for the temperature range $320^{\circ}$-$760^{\circ}$K.

Extension of this $C_p^{\,o}$-function beyond the experimental
temperature limits of the calorimetric measurements to the average tempera-
ture used in the vaporization studies ($960^{\circ}$K) is safe since $C_p^{\,o}$ is only
slightly temperature dependent. The total error introduced using the $C_p^{\,o}$-
function between $298^{\circ}$ and $960^{\circ}$K is less than 0.3 kcal.

With the experimentally determined heat capacity the vapor pressure measurements on CdSe have been evaluated using the second-law and third-law techniques. Thermodynamic values have been obtained for the enthalpy and entropy of vaporization, for the heat of formation of CdSe, and for the absolute entropy of CdSe. The results are critically compared to vapor pressure data obtained by other techniques. These calorimetric and thermodynamic studies on cadmium selenide are now being prepared for publication.

The thermodynamic investigations of vaporization processes are extended to the manganese-tellurium system.

## CRYSTALLIZATION DURING POLYMERIZATION

Senior Investigator:    B. Wunderlich

Further work on the simultaneous polymerization and crystallization of polyparaxylylene has been carried out. All information points to the fact that our present knowledge is insufficient to explain the detailed chemical reaction. Attempts to seed this reaction above a certain critical temperature of $30^{\circ}C$ have failed. Crystal structures achieved seem not to be of the extended chain nature. From general knowledge of crystallization during polymerization this must mean that before final achievement of crystallization a period of mobility of already polymerized molecules must exist. At present the relatively large experimental material developed over the last two years is being collected and surveyed for possible clues of further work in this direction.

The other polymeric system under investigation, polymetaphosphates, in contrast show very clearly extended chain crystals with high molecular weight without any chain folding. Electron micrographs of fracture surfaces show identical surface morphologies as the previously analyzed extended chain crystals of polymers, namely polyethylene, polytetrafluoroethylene and selenium.

Overall it seems to show that the two polymer systems chosen illustrate clearly the added difficulties encountered in detailed evaluation of polymerization reactions which occur when crystallization can occur simultaneously.

ELECTRON OPTICS INSTRUMENTATION STUDIES OF SOLID STATE REACTIONS

Senior Investigator:       G. Judd

The emphasis of this project has been to correlate the corrosion and mechanical properties of certain precipitation hardenable aluminum alloys to the presence of "precipitate free zones" (PFZ) which these alloys exhibit in aged condition. These PFZ are thought to be the sites of extensive work hardening and initial crack nucleation during plastic deformation. The immense practical importance of stress corrosion in high strength aluminum base air craft alloys necessitates a thorough and more basic study of the PFZ and their effect on corrosion and mechanical properties.

In the present investigation, several aluminum base alloys that had been examined by transmission electron microscopy in earlier reported work to reveal the effect of ageing treatment on the substructure, precipitate morphology, and PFZ characteristics were subjected to extensive electron probe microanalysis. The microanalysis studies established solute profile for each of the alloys. It was found that within a given alloy that solute enrichment and solute depletion could either or both occur depending upon the quenching and ageing treatment and the grain boundary studied. Further in some grain boundaries no segregation at all was observed. These results are now being correlated with the morphology of the PFZ as observed by electron microscopy to obtain an explanation of the structure and composition observations.

In addition, work has also begun to study the occurrence of pitting corrosion in stainless steels. These samples will be observed to study this type of corrosion attack by electron microscopy and electron probe microanalysis to determine if there is a chemical microsegregation responsible for a favorable pit nucleation site.

# NUCLEAR MAGNETIC RESONANCE

Senior Investigator:    P. A. Casabella

The temperature dependence of the $Na^{23}$ nuclear quadrupole coupling constant has been studied in both non-ferroelectric phases of Rochelle salt. A plot of the $Na^{23}$ coupling constant vs. temperature shows that all the measured values in the non-ferroelectric phases fall on the same straight line. In the ferroelectric phase, from $-18^{o}$ to $+24^{o}C$, there are two different coupling constants split symmetrically above and below the straight line.

This data casts doubt on a previously accepted model for the mechanism of ferroelectricity in Rochelle salt. It had been assumed that the temperature dependence of the $Na^{23}$ coupling constant was much weaker than that revealed by these measurements. Therefore, the difference between coupling constant measured just above and just below the ferroelectric range was attributed to a difference of phase between the two temperature ranges. This phase difference was believed to imply an anti-ferroelectric low temperature phase. Furthermore, the ferroelectricity was believed to be due to a polarization of one half of each unit cell of the crystal. However, the symmetrical splitting of the quadrupole coupling constants in the ferroelectric phase seems to argue against this. Previously, with the implicit assumption of a weak temperature dependence of the $Na^{23}$ coupling constant the model seemed to fit the data quite well.

At this point it is not clear whether some other model might fit the data better, but the matter will remain under study.

# MECHANICAL PROPERTIES AND STRENGTHENING MECHANISMS

N71-19729

Thirteen projects in this area of materials studies embrace research on the behavior of a variety of metal alloys, polymers and composites. Some highlights from recent work covered in the following reports include:

Unique observations of effects on crack path in beta brass embrittled in a liquid metal environment.

Potential new insights on the fracture of alloyed ferrites from observations on high purity ferrite.

Torsion test results on Al-Zn eutectoids which may open a means of characterizing superplasticity.

Development of a thermal shock method for studying the role of localized stresses in dispersion strengthening.

Observations which specifically associate low shear strengths with surface orientation in the structure of high modulus graphite fibers used in composites.

Thermoelastic data which suggest an inverse relationship between crystal size and large deformation elasticity in polyethylene.

Unique, large deformation, cyclic, stress-strain data on polyethylene indicating that after an initial yielding this material can be conditioned to cyclic repetition of large strains.

Data demonstrating that judicious substitution of functional groups in butadiene based polymers can significantly influence flow properties such as bulk viscosity and temperature coefficient of flow.

PLASTIC DEFORMATION AND FRACTURE OF BETA BRASS ALLOYS

Senior Investigator:     N. S. Stoloff

The purpose of this investigation is to determine the influence of solid solution additions of nickel or manganese on the ordering energy and plastic deformation of β CuZn alloys.

A peak in flow stress is found for polycrystalline binary Cu-Zn alloys at 175°C. Ni lowers the temperature of the peak, while Mn raises that temperature. Mn is a more effective solid solution strengthener than is Ni at all test temperatures. For all alloys there is an abrupt change in slip mode in the vicinity of the peak. Glide changes from diffuse, wavy slip to well defined straight slip bands just below the temperature of the peak. Studies of single crystals suggest that there is a change in slip vector from <111> at low temperatures to <100> in the vicinity of the peak.

Since all polycrystalline alloys were highly ductile in air, thereby precluding study of brittle fracture phenomena, an extensive study has been made of the effects of liquid metals and aqueous ammonia environments on fracture. Susceptibility of β CuZn to liquid metal embrittlement by gallium, indium or mercury is raised by Mn solid solution additions. Embrittlement by gallium is transgranular, while the other liquid metals produce intergranular failure. This behavior appears to be unique in that the crack path of most metals is unaffected by the nature of the liquid metal. Cracking in all alloys tested in aqueous ammonia was transcrystalline.

Cleavage occurs along {100} in gallium-embrittled binary Cu-Zn; alloys containing Mn appear to cleave on a {310} plane. Ni has

no effect on the cleavage plane.

The ordering temperature, Tc, of all alloys has been determined through yield stress vs. temperature studies. Mn lowers Tc, while Ni raises it. The changes in Tc can be correlated with the effects of the alloying elements on plastic deformation.

Single crystals of binary and ternary alloys have been tested between room temperature and $200^{\circ}C$ to study the influence of temperature on slip systems, critical resolved shear stresses work hardening rates and the occurrence of serrated yielding. The results of these studies are now being evaluated.

## DEFORMATION AND FRACTURE OF DIRECTIONALLY SOLIDIFIED EUTECTICS

Senior Investigator:     N. S. Stoloff


This is a program to determine the effectiveness of intermetallic compounds as reinforcing phases for high temperature composite applications.

Assembly of an apparatus for passing eutectic alloys through a steep temperature gradient during solidification is complete. An ingot of AgMg has been grown successfully at a rate of 5.4"/hr. Modification of the apparatus to increase the temperature gradient so that ingots can be grown at rates of 50"/hr is underway. Upon preparation of a sufficient number of specimens, the effect of growth rate on spacing of phases and on mechanical properties will be determined.

Initial attempts to prepare ingots of an Ag-Al eutectic were unsuccessful due to reaction of aluminum with the graphite crucible. Alumina or crystalon crucibles have since been found to be suitable for this alloy.

FRACTURE OF ALLOYED FERRITE

Senior Investigator:     N. S. Stoloff

The effects of substitutional solutes on the plasticity
of high purity ferrite are being studied.  Purification of an Fe-5%Cr
alloy by $ZrH_2$-gettered $H_2$ gas has been accomplished.  Tensile specimens
of this alloy have been tested in both the recrystallized and as rolled
conditions between $-196^{\circ}C$ and $300^{\circ}C$.  The results are to be compared
with purified unalloyed iron to determine whether purification of
interstitials reduces or eliminates the alloy softening effect found
in most bcc alloys.

Another approach to purification of iron, through the use
of vanadium solid solution additions, has been successfully completed.
While unalloyed iron reveals ageing phenomena at room and elevated tempera-
tures, no such ageing effects were found in Fe-V alloys.  Also, cooling
rate had a large effect on ductility in unalloyed iron, but no effect
was noted in Fe-V alloys.  Apart from sharply lowering interstitial
contents, vanadium supresses cross slip, and consequently lowers the
ductility of ferrite.  However, these harmful effects can be mitigated
by the use of thermal recovery heat treatments to produce a stable
substructure.

The ductile to brittle transition in both Fe and Fe-V
alloys was shown to be related to the onset of planar glide due to
restricted cross slip at low temperatures.  Restricted cross slip also
accounted for an increased incidence of twinning in high vanadium alloys.
These observations could be explained by a modified Cottrell-Petch theory
of fracture, in which slip mode is shown to influence ductility through
a change in stress concentrations at grain boundaries.

# SUPERPLASTICITY

Senior Investigator:     L. Jackman

The purpose of this investigation is to determine the mechanism responsible for superplasticity, which refers to the ability of some metallic materials to exhibit unusually large elongations of up to 2000 per cent under uniaxial loading. The internal fraction spectrum has been determined for the Al-Zn superplastic eutectoid alloy over the temperature range from -160 to $130^{\circ}$C for two frequencies. No internal friction peaks were observed, but the background damping was significantly greater than has been reported for other metals and alloys. The variation of shear modulus with temperature was also determined and was consistent with the temperature variation of the damping ratio. The average activation energy associated with the background damping was about 22,000 Cal/mole$^{\circ}$K, which is the same value found for this alloy while undergoing uniaxial deformation in the superplastic range.

In order to further establish the relationship between background damping and superplastic deformation, the effect of grain size is being determined. A small grain size is the primary prerequisite for superplasticity. Although neither heat treatment nor uniaxial deformation produce significant grain growth, torsion deformation in the superplastic range has been observed to induce substantial grain growth. Specimens previously deformed in torsion to promote grain growth are presently being subjected to internal friction measurements. The background damping decreases substantially with increasing grain size but no peaks in the internal friction spectrum have emerged.

Internal friction measurements are also being performed on the Zn-Al eutectoid alloy with a laminated structure for comparison with the equiaxed grain structure characteristic of superplastic alloys. Effects of composition on the damping behavior and their relation to superplastic behavior will also be examined.

An inverted torsion pendulum apparatus with a frequency in the 1 cps range has been built to measure the damping ratio (logarithmic decrement) and the shear modulus. Torsion deformation is imparted with a verticle torsion apparatus capable of a wide range of strain rates and very close temperature control. The torsion behavior of superplastic materials will be further characterized.

SILVER-GALLIUM OXIDE ALLOYS

<div align="center">Senior Investigator:    F. V. Lenel</div>

A dispersion strengthened alloy of silver 1 mole per cent gallium oxide was prepared by two different techniques. The first technique developed specifically for this investigation entailed freeze-drying and subsequent reduction of silver-gallium nitrates to silver and gallium oxide followed by pressing and sintering of the powder mixture. The second technique was the internal oxidation of a silver 1 a% gallium solid solution alloy under condition which yielded a uniform dispersion of oxide through the specimen cross-section. The structure of both types of alloy was determined. There was no significant difference between the average particle size and the particle spacing of the second phase in both types of alloy. However, the grain size of the internally oxidized type was 40 times larger than the grain size of the consolidated powder type of alloy. The steady state creep rates for the fine grained consolidated powder mixture and the coarse grained internally oxidized alloys were measured in the temperature ranges of 706 to 826°C and 698 to 796°C, respectively, and in the stress ranges of 100 to 350 psi and 100 to 1000 psi, respectively.

The steady state creep rates of the consolidated powder mixture followed the relation:

$$\dot{\epsilon}_s = A \exp\left(\frac{-Q}{RT}\right) \exp\left(\frac{B\sigma}{RT}\right)$$

where $\dot{\epsilon}_s$ is the steady state creep rate, A and B are constants, $\sigma$ is the applied stress, R is the gas constant, and T is the test temperature in degrees absolute. The activation energy for creep, Q, is quite high and appeared to be stress dependent. It is 252 KCal/mole at a stress of 100 psi, and 221 KCal/mole at 320 psi.

The same results for fine grained consolidated powder could be represented by the equation:

$$\dot{\epsilon}_s = A \; \sigma^n \; \exp\left(\frac{-Q}{RT}\right)$$

where n is constant of about 12.6. The average activation energy for creep, Q, was found to be 236.3 KCal/mole.

It is proposed that the controlling mechanism for steady state creep, in the fine grained alloy produced from the consolidated powder mixture, is the generation of dislocations from the grain boundaries.

The steady state creep rates of the coarse grained internally oxidized alloy was proportional to the stress up to a stress of 500 psi, and proportional to the fourth power of the stress at high stresses. The activation energy for creep was stress independent and agreed very well with the activation energy for self-diffusion in pure silver.

It is proposed that the rate controlling mechanism for steady state creep in the coarse grained internally oxidized alloy is a diffusion controlled dislocation climb process.

In the continuation of this study it is planned to produce internally oxidized silver-gallium oxide alloys with a fine grain structure, in order to compare the creep rates of internally oxidized and powder metallurgy alloys which are similar not only in the size and shape of the oxide particle, but also in grain structure.

Conclusions from the work to date are:

1. Dispersion strengthened single crystal alloys of silver containing a uniform dispersion of gallium oxide can be produced

in sheet form by internal oxidation utilizing an oxidation schedule in which the oxygen partial pressure is increased with the square of time maintaining a constant oxidation front velocity.

2.   Comparison of the variation of critical resolved shear stress with microstructural parameters and the predictions based on the theoretical models proposed to account for the yielding behavior of dispersion strengthened alloys was inconclusive.  It was found that both bowing and particle shear models satisfactorily but not uniquely described the observed yielding behavior.

3.   The observed work hardening behavior of this alloy series was consistent with previous observations of Ebeling and Ashby for a series of copper-silica alloys.

Detailed reports of this work have been published during the report period in theses of M. Y. Nazmy and K. C. Wang.

NOTE

The experimental work on sintered aluminum alloy powder has been completed, and a comprehensive report is being prepared.

## DISPERSION STRENGTHENING MECHANISMS

Senior Investigator:     G. S. Ansell

This research program is concerned with the effects of second-phase particles on the physical and mechanical properties of crystalline solids. During this program period, studies were continued concerning the effect of localized stress state around second-phase particles upon the mechanical properties of two-phase alloys. We have focussed on the use of thermal shock as a method of inducing interface stress in nickel-thoria alloys. Here the experimental approach has been to rapidly heat specimens to temperatures ranging from 500 to $1400^{o}F$ followed by immediately performing a tensile test at elevated temperature. The thermal rise coupled with the difference in thermal expansion coefficient between the thoria particle and nickel matrix stresses the interface while the subsequent testing indicates whether interface failure thus results. This method permits direct determination of the particle-matrix interfacial bond strength in two-phase alloys. Continuing studies in this area are in progress.

# GRAPHITE FIBER-EPOXY COMPOSITES

Senior Investigator:      R. J. Diefendorf

Composites of high strength and modulus carbon fibers embedded in epoxy have been design limited by their shear strengths. The purpose of this investigation was to determine the cause of the poor shear strengths. Shear strengths were evaluated by loading composite beams with the fibers aligned parallel to the beam axis under three point loading conditions. The shear strength decreases as the fiber modulus is increased. An increase in fiber modulus from 25 to 50 million psi decreases the composite shear strength from 12 to 2 ksi. The failures were shear at the mid-plane and not tension or compression at the surface. Fracture analyses on the samples indicated that the fiber matrix interface was failing. Thus, the carbon fibers' surfaces are changing the composite strengths.

The microstructures of the fibers were studied to determine how the surface was changing. The modulus of the polycrystalline fibers depends on the orientation of the anisotropic graphite crystallites. As the strong basal planes become more parallel to the fiber axis, the fiber modulus increases. However, the fiber surface energy and shear strength are governed by the way the basal planes intersect the fiber surface. Since two lines are needed to determine a plane, the basal planes can be parallel to the fiber axis, and be either normal or parallel to the fiber surface. The microstructure of several varieties of carbon fibers were completely characterized. Fibers from both polyacrylonitrile and cellulose were analyzed.

The poor penetrating power of electrons, about .2 microns on a 10 micron diameter fiber, allowed surface electron diffraction and

dark field electron microscopy to reveal that the basal planes on the surface were parallel to the surface. Surface dark field microscopy and electron diffraction also yielded information about the interlayer spacing, crystallite size, and preferred orientation of the basal planes with respect to the fiber axis. X-rays due to their complete penetrating power yielded the same information about the (core) average fiber properties. These average values for x-rays were compared to the surface values obtained to see if the surface was different from the core. The comparison showed that the surface graphite had lower interlayer spacing, larger crystallite size and a higher degree of alignment of the basal planes with respect to the fiber axis. This indicated that the surface was more graphitic and, hence, had lower than average shear strength. The x-rays are not sensitive to the radial fiber structure, so polarized light microscopy on polished cross section was utilized for this. The structural observations indicated that the polyacrylonitrile based carbon fibers had structures similar to that of a tree trunk. Rayon based fibers had random interiors but had skins on the surface, with the basal planes parallel to the surface. These structures both had basal surfaces which have relatively low surface energy, thus causing poor wetting and adhesion. The surfaces also have low interlaminar shear strengths, so even if wetting and adhesion are adequate the surface will fail by interlaminar shear. Which of these two failure mechanisms prevailed could not be determined, but the structure of the interface is now known and steps can be taken to correct the problem.

BIAXIAL VISCOELASTIC STUDIES

<div align="center">Senior Investigator:     S. S. Sternstein</div>

Yielding and crazing studies on glassy high polymers under multiaxial stress states have shown that plastic deformation in these materials is governed by stress field criteria which depend on the isotropic component of the stress tensor. For example, the octahedral shear stress required for a shear yielding mode has been shown to decrease linearly with increasing first stress invariant (or mean normal stress), whereas the stress bias required for a crazing mode increases with the reciprocal of the first stress invariant. These results have been applied successfully to the toughening phenomenon in rubber modified, glassy high polymers.

In order to determine the effect of multiaxial stress states on the general viscoelastic-plastic behavior of high polymers, it is essential to study viscoelastic response in combined stress fields. Questions to be resolved include: Does stress component coupling exist in the linear viscoelastic region? Is shear relaxation equivalent kinetically to tensile relaxation? To answer these questions, several pieces of apparatus are now under construction. The first apparatus is designed to study simultaneous relaxation of tensile and torsional stresses in rigid high polymers. Other equipment are being constructed to study torsional and tensile relaxation independently and with high precision.

Both homopolymers and two phase systems will be studied, including rubber modified glasses and filled elastomers. Preliminary data indicate that stress concentration effects due to a second phase play an important role in determining the kinetics of viscoelastic response.

# MORPHOLOGY OF COLD-DRAWN POLYMERS

Senior Investigator:     D. Hansen

So called rubber elastic behavior is a distinctly dif-
ferent phenomenon from the elastic behavior of rigid materials.  It
applies over large deformations and is associated with changes in
entropy rather than the internal energy of the material.  Rubber
elasticity is an important aspect of the behavior of linear high polymer
materials and, structurally, is attributed to the ability of the large
molecules to assume a variety of different conformational states.

Highly crystalline polymers, like polyethylene, also
exhibit characteristics of rubber elasticity but it is not so clear how
this relates to structure.  The crystalline structure does not offer
the same conformational freedom that is available in an amorphous rub-
ber.  We have hypothesized that the long-range elasticity in crystalline
polymers arises from the large interfaces between small crystals which
offer the potential for large changes in interfacial free energy or
interfacial entropy on deformation.

To test this hypothesis, and more generally to look at
relationships of crystal morphology to mechanical behavior, we prepared
and tested a series of polyethylene samples crystallized under specifically
controlled conditions.  The first set of samples was prepared by
crystallizing at different temperatures to yield different size
(lamellar thickness) crystals.  All specimens were, however, prepared
with the same density ($0.97$ gms/cm$^3$).  Mechanical testing was by cold-
drawing to a strain of 4 followed by creep and relaxation tests.  The
results of these tests were quantitatively in agreement with the above
hypothesis.

#2

In another series, specimens of fixed crystal size but different densities were prepared and tested. The results of this series indicated a more complex behavior suggesting transformations of unstable structures during deformation. Evaluation of these data is not yet complete.

# KINETICS OF DEFORMATION OF CRYSTALLINE POLYMERS

Senior Investigator:     D. Hansen

Crystalline polymers can be subjected to large deformation (several hundred percent) which orients the structure and dramatically alters the properties. Specific use of this behavior is made in the drawing of fibers and films. Much research has been done on the drawing process and associated treatments such as annealing which are used to stabilize oriented crystalline polymers. Investigations of the properties of these materials indicate strong interactions of temperature and stress in both reversible and irreversible responses.

To probe this behavior in a new way we designed an experimental system which would permit cyclic deformations at large strains. We have done this with an apparatus which deforms the material in simple shear. The following figure (Figure 6) illustrates the capability of this apparatus. The data reproduced in the figure were obtained on a linear polyethylene specimen at $60^{\circ}$C. The curve labeled "A" is the stress strain relationship for the original deformation. At a strain of 4 the deformation was reversed until an equal strain in the opposite direction was achieved. This cycle was then repeated four times with the results indicated by the curves "B". Following this four cycles between strain limits of $\pm$ 3 were done yielding curve "C".

The most striking, and somewhat unexpected, feature observed in this test was that deformation cycles after the first were repeatable. This establishes that the cycling technique can be used to separate, in large measure, permanent changes from mechanically reversible deformations. We are proceeding with further testing of polyethylene at different strain rates and temperatures in order to assess the interactions of time, temperature and stress.

MARLEX 5003

$T_0 = 60°$ C
$R_0 - 4$ cycles
$R_1 - 4$ cycles

FIGURE 6
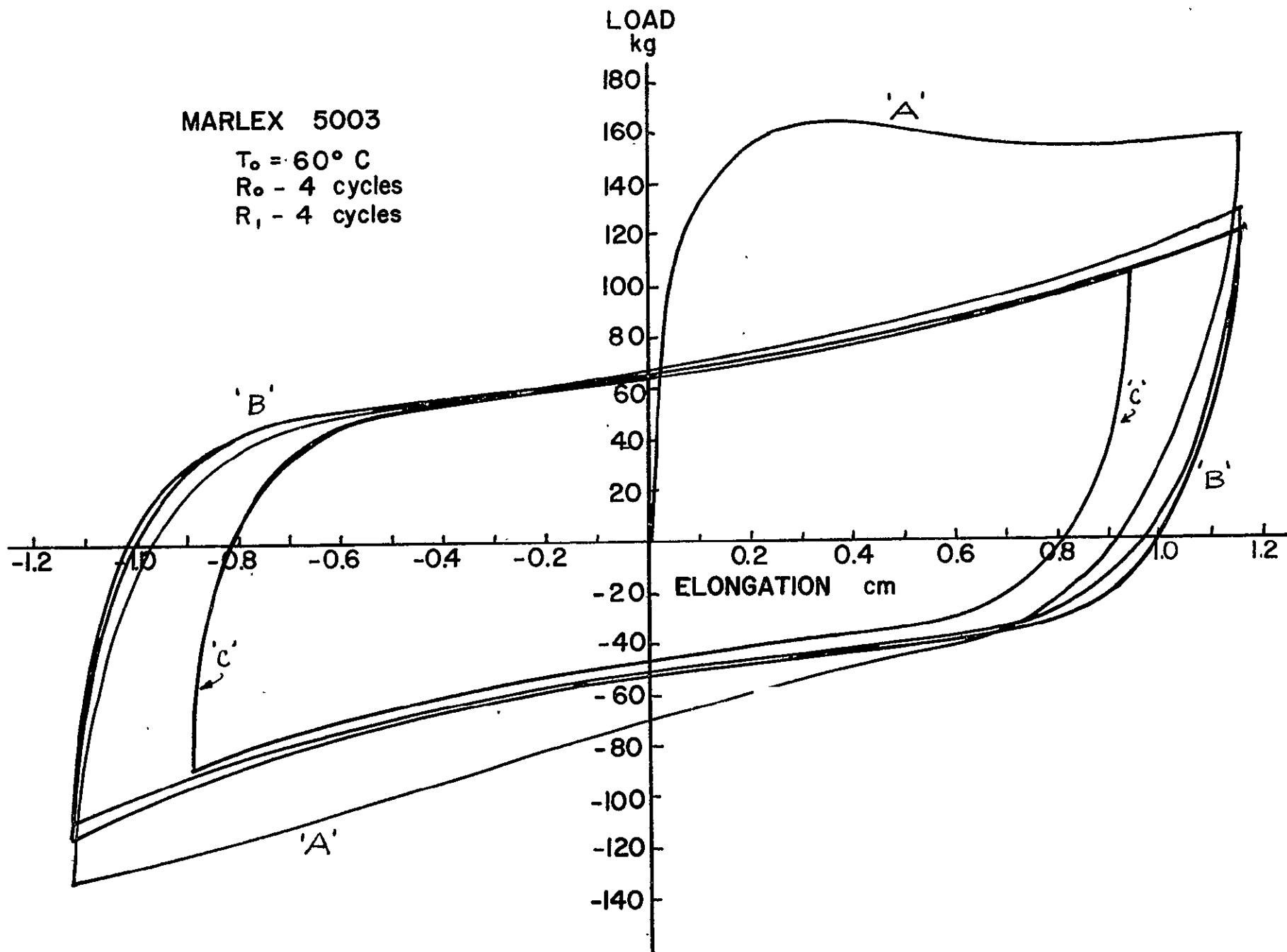
THE RELATION OF MOLECULAR STRUCTURE TO THE FLOW OF POLYMERS AND POLYMER DISPERSIONS AS A FUNCTION OF TEMPERATURE AND SHEAR RATE

Senior Investigator:     W. H. Bauer

Investigations of the flow properties of bulk polymers based upon polybutadiene with a variety of functional groups such as carboxyl, hydroxyl and nitrile have shown that the limiting viscosities of the butadiene polymers may be varied over a very wide range at the same molecular weight by proper choice of the functional group. It was found that a wide range of temperature coefficients of flow was produced by the change of functional groups. Such groups as carboxyl give very high relative limiting viscosities and very high comparative temperature coefficients of flow. From these results it is clear that proper choice of functional groups enables a very large change of bulk viscosity to be produced in butadienes in the molecular weight range of from 3 to 10,000. Work is being continued to enable measurements made in solution to be related to the bulk polymer studies.

## FLOW OF NON-NEWTONIAN FLUIDS

Senior Investigator:      S. J. Kurtz

The principal aim of this investigation is to use certain
simple non-viscometric flows, i.e., radial flow as found in injection
molding and the orthogonal rheometer flow, to study non-Newtonian
fluids. An apparatus has been designed and built to investigate the
velocity and pressure distribution in radial flow. No data have been
taken so far. The orthogonal rheometer is now operating and experimental
values for standard viscosities of Newtonian fluids agree within a 1%
error. Preliminary work on some "Bingham fluids" indicates a yield
value in the orthogonal rheometer at a strain near 0.03. This requires
a sensitivity of better than 1 gram-force which is close to the lower
limit of this instrument.

A complimentary study on the flow field in the orthogonal
rheometer is being conducted simultaneously. An instrument has been
set up to photograph tracer particles in the flow field. This project
is scheduled to be completed at the end of this academic year.

ELECTRONIC AND PHYSICAL PROPERTIES OF MATERIALS

The work in this section deals mainly with thermal and elastic properties of polymers, and the electronic properties of glasses and metals. Thermal capacities of polymers are being measured at temperatures above the melting point, where there appears to be an unexpected influence of pre-melted history, and at liquid $He_3$ temperatures, where the emphasis is on that portion coming from local modes. This quantity appears as an excess over the Debye contribution which is determined by ultrasonic measurements of elastic wave velocities. Studies of thermal conductivity are also being made at high temperatures to investigate anisotropy in specially prepared polymer crystals and in addition in low temperature regime as well.

Relaxation technique has been applied to glasses doped with iron oxides to explore the conduction mechanism. There appears to be some evidence of electron hopping. Mössbauer measurements of internal, hyperfine magnetic fields are being applied to solutions of iron in zinc to explore spin fluctuation in this non-magnetic system and studies of iron in the molybdenum-niobium system are being used to determine the onset of magnetic moment as a function of composition.

## HEAT CAPACITY OF SOLID POLYMERS

Senior Investigator:      B. Wunderlich


The first measurements of heat capacities on amorphous polyethylene have been completed. The region available for measurement stretches from approximately $130^{\circ}$ to $300^{\circ}C$. Almost over the whole range the measured heat capacities were shown to be linear. As outlined previously, this linear heat capacity is in contrast to the present theoretical estimations of the heat capacity of amorphous polyethylene. In addition, it was discovered that the heat capacity in the amorphous region seems to be dependent upon the thermal pre-treatment. Polymer melts produced from highly crystalline polymers seem to have a lower heat capacity than polymer melts produced from a less highly crystalline material. This result is extremely surprising since one would expect that in the melt all thermal history is erased quickly. At present a thorough investigation of equipment and material is underway to insure that the observed effect is not due to a systematic error.

Initial inquiry into the possibility of storing heat capacity data on computer tape has been made. It is hoped that in the future a system can be developed to store a body of up-to-date heat capacity information on all polymeric materials.

THERMAL CONDUCTIVITY OF CRYSTALLINE POLYMERS

Senior Investigator:     D. Hansen

A polymer crystallized from the melt is a composite of very small crystals and the crystal interfaces and/or amorphous material. It is expected that the anisotropic structure of the crystals should be reflected in a highly anisotropic thermal conductivity. In a macroscopic specimen thermal conductivity is sensitive to crystal size and orientation. In seeking to delineate these relationships quantitatively we are measuring thermal conductivities of specially prepared specimens including specimens crystallized at different temperatures (to control crystal size), specimens prepared by annealing single crystal mats (for extreme orientation), and specimens with intermediate degrees of orientation.

Specimens with different degrees of orientation may be prepared by mechanical drawing or by crystallization in a temperature gradient field. Mechanical drawing causes complex structural changes and produces a specimen which is dimensionally unstable and not well suited to this thermal conductivity study. Controlled crystallization in a temperature gradient has been performed by researchers using adaptations of zone melting procedures. This is a tedious process and the control of temperature at the crystallization front is poor. In view of this we undertook the development of an apparatus which permits crystallization while maintaining a fixed temperature gradient. The technique should, however, be more widely useful for preparing stable, oriented polymer specimens and for studying polymer crystallization.

The apparatus is indicated schematically at the top of
the following figure (Figure 7). It is simply two metal (brass) blocks
fitted with coils for heating and cooling. The specimen is sandwiched
between the blocks which are then heated to temperatures above the
melting point of the polymer. Cooling of the blocks is then performed
at a constant rate maintaining a fixed temperature difference between
the blocks as indicated in the lower part of the figure. The temperature
gradient is controlled by the selection of $\Delta T$ and the specimen thickness.
·Because the rate of crystallization of polymers is temperature sensitive,
increasing with decreasing temperature, the rate of cooling is able to
control the crystallization temperature.

Using a polyethylene specimen 1/16 inch thick with a $\Delta T$
of $50^{\circ}C$ and a cooling rate of approximately $5^{\circ}C/hour$, we have prepared
a specimen of orientation at least equal to that achieved by zone melting
techniques. Work on the apparatus and technique is proceeding to extend
its range of operation to larger gradients and to prepare a set of specimens
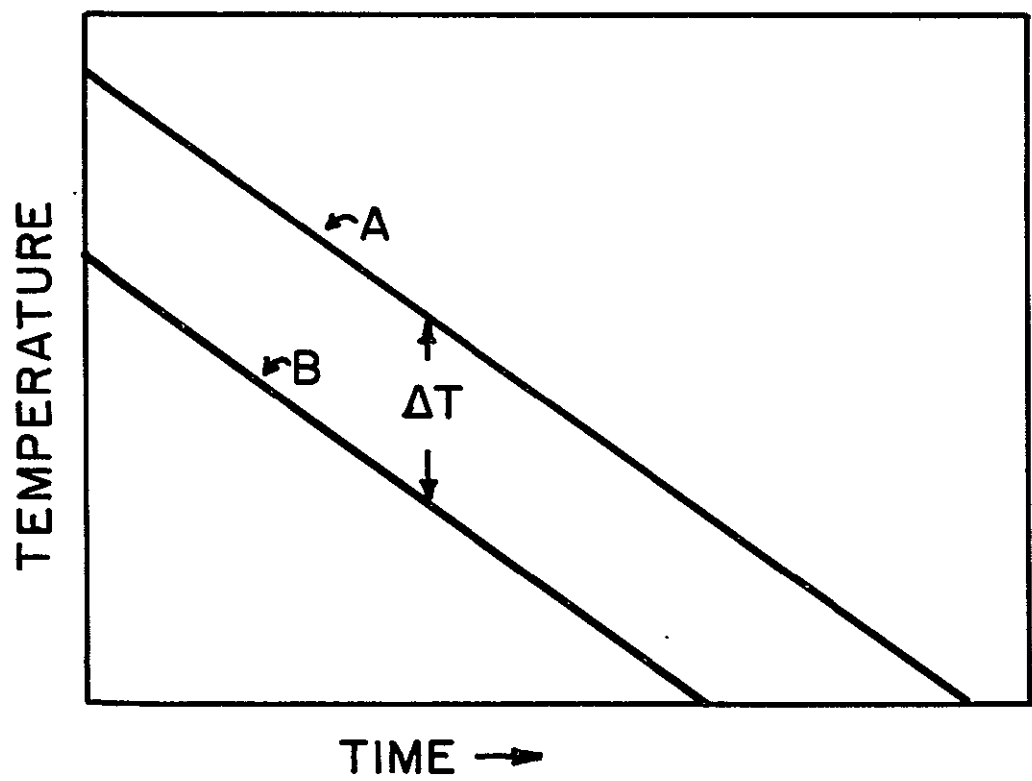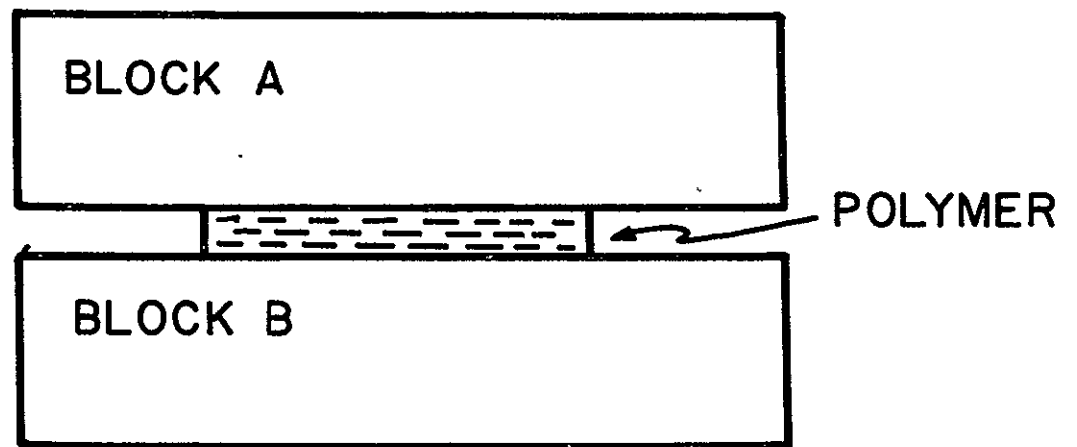for the thermal conductivity study.

BLOCK A

POLYMER

BLOCK B

FIGURE 7

## LOW TEMPERATURE THERMAL CONDUCTIVITY OF AMORPHOUS SOLIDS

Senior Investigator:     G. L. Salinger

The specific heat of polyethylene has been measured between 0.4 and $4^{\circ}K$ for a variety of crystallinities. In general, the specific heat at a given temperature decreases with crystallinity. This is consistent with the excess specific heat being due to localized modes due to motion of pendant groups (branches) in voids in the amorphous phase.

Above $2^{\circ}K$ the specific heat of a sample crystallized under pressure (5000 psi) is much less than the specific heat of a sample crystallized at low pressures. The densities and hence the crystallinities of the two samples are very close. This experiment supports the hypothesis that the localized modes are pendant groups oscillating near voids. In general, the excess specific heat can be accounted for by assuming that only a fraction of a percent of all the modes are localized modes. The pressure collapses some of the voids, pinning the oscillator. This would produce only a small change in density, but a large change in the specific heat.

Below $1^{\circ}K$, the value of $c/T^3$ increases for samples made under pressure. This increase seems to be more dependent upon crystallinity than on pressure.

Sound velocity measurements are being made to determine the Debye contribution to the specific heat so that we can calculate the frequency and strength of the localized modes.

Measurements of the thermal conductivity of carbons of various heat treatments are being continued. At present we are gathering data before trying to explain the temperature dependence.

LOW TEMPERATURE ACOUSTIC MEASUREMENTS IN POLYMERS

Senior Investigator:    G. L. Salinger

The pulsed echo technique of measuring the velocity of propagation of polarized 10 MHz sound waves through step-shaped polymer samples has been extended to a variety of polymers. The resulting velocities are being used to determine the Debye contribution to the specific heat of polymers at low temperatures. In addition, the bulk modulus, Young's modulus, the shear modulus and Poisson's ratio can be determined to give some idea of the elastic strength of the material at low temperatures. There are three main avenues of investigation.

We have measured the velocity of polarized 10 MHz sound waves in two technical polymers, nylon and Teflon, and two epoxy resins, Epibond 100A and Epibond 121 (Furane Plastics Company). These were chosen because published values of the calorimetrically measured specific heat were extrapolated to $0^{o}K$ using a Debye $T^3$ law. As can be seen in the table, $c/T^3$, measured acoustically is in general much less than that measured calorimetrically because of localized modes contributing to the calorimetric specific heat of polymers.

|  | Nylon | Teflon | Epibond 100A | Epibond 121 |
|---|---|---|---|---|
| $c/T^3$* acoustic $0^{o}K$ | 153 | 337 | 188 | 166 |
| $c/T^3$* calorimetric $0^{o}K$ | 190 256 | 890 900 982 | 291 283 | 235 |

*The units of $c/T^3$ are ergs $gm^{-1}$ $^{o}K^{-4}$.

Thus, it is very dangerous to extrapolate calorimetric specific heat measurements to lower temperature. In this study the various moduli have also been determined.

In a second study the velocity of polarized sound waves has been measured in polymethyl methacrylate and polystyrene. These were initially performed to help us determine the frequency and strength of the localized oscillators as determined by our calorimetric specific heat measurements. As a result of more careful sound velocity measurements we have found that the excess specific heat of polystyrene is still about 50% of the total specific heat at $1^{\circ}$K. The low temperature increase in $c/T^3$ must be taken seriously with a resultant change in the frequency of the higher temperature modes. The temperature dependence of Young's modulus calculated from our velocity measurements is in excellent agreement with more accurate internal friction measurements by Dr. MacCrone's group. The sound velocity of polystyrene is not temperature independent at $4^{\circ}$K. We plan to investigate this point. Gruneisen constants will be extracted from the data.

In the third study we use sound velocity measurements to determine the Debye contribution to the specific heat of the amorphous and crystalline portions of polyethylene. Measurements to date indicate values of the Gruneisen constant between 3 and 4 in agreement with an earlier surmise of Reese.

Financial support for these projects is also received from the National Science Foundation and the Office of Naval Research.

## IONIC DEFECTS AND ELECTRONIC PROPERTIES OF TRANSITION METAL OXIDES

Senior Investigator:     R. K. MacCrone

The purpose of this research is to investigate polaron hopping and polaron states in transition metal oxides, particularly NiO doped with monovalent impurity, namely Li.

Dielectric relaxation measurements have been made for pure NiO crystal and for Li-doped NiO crystal between $2^{\circ}K$ and $300^{\circ}K$. Analysis of the results are currently being made. Low temperature measurements indicate the effect of the stress on the dielectric behavior. Possible explanations for this are: (1) variation of the contact resistance between crystal and the electrode, and (2) variation of the spin state by the stress.

Experiments to resolve this problem are planned.

SEMI-CONDUCTION IN GLASS

<div style="text-align:center">Senior Investigator:    R. K. MacCrone</div>

The dielectric and mechanical properties of PbO-SiO$_2$ glasses containing FeO and Fe$_2$O$_3$ are under investigation at temperatures of 300°K to 500°K. Concentrations of FeO and Fe$_2$O$_3$ vary from 0 to 10 mole percent.

A.C. measurements in this temperature range indicate the presence of a distinct dielectric relaxation at 400°K. The strength of this relaxation increases with increasing iron concentration. Present work is aimed at determining whether this phenomenon is ionic or electronic in nature. Experimental study of potential gradients applied to the glass appears to eliminate the possibility that the relaxation is caused by surface effects. Determination of the Fe$^{+2}$/Fe$^{+3}$ ratio by chemical analysis is in progress and attempts at varying this ratio in the glass to determine its effect on the dielectric properties are being made.

Preliminary application of existing theory to experimental results indicates conduction by means of a hopping process with polaron effects present. Further necessary theoretical and experimental investigation to verify this observation and determine the exact nature of conduction is presently proceeding.

Internal friction measurements of these glasses indicated the presence of a mechanical relaxation at approximately the same temperature as the dielectric relaxation. At present, theoretical analysis to determine whether or not a relationship between the dielectric and mechanical relaxations exists is in progress and experiments along this line are planned.

Investigation of dielectric properties in $BaO-B_2O_3-SiO_2$ glasses containing titanium ions has been initiated to determine if polaron hopping occurs in this system. Glasses containing $Ti^{+3}$ and $Ti^{+4}$ from 0 to 30 mole percent are being made and measurements of the 0% composition are in progress. The $Ti^{+3}/Ti^{+4}$ ratio can be accurately controlled in this glass.

## ULTRASONIC STUDIES OF GRANULAR MIXTURES

Senior Investigator:     S. Katz

Many types of rock, with porosities in the form of cracks in the range of 0.05 to 1%, have elastic wave velocities which are 20% less than the value when the porosity has been reduced to zero under high hydrostatic pressure or full fluid saturation. A theory which partially predicts the large increase in elastic wave velocities and elastic constants due to fluid saturation of such a material has appeared in the literature, but remains untested over a wide range of fluid saturation. Experiments have been initiated to test this theory and to provide data for improving it.

# LOW TEMPERATURE MAGNETIC PROPERTIES OF DILUTE ALLOY SYSTEMS

Senior Investigator:    M. P. Maley

Mössbauer effect measurements have commenced on the magnetic behavior of very dilute Fe impurities in Zn metal. Recent transport measurements have indicated the presence of small localized magnetic moments on the Fe atoms. This phenomenon has not been detected by macroscopic susceptibility measurements. The Mössbauer effect offers the possibility of investigating microscopically the local electronic magnetic behavior by looking at the hyperfine field at the $Fe^{57}$ nucleus.

Measurements are taken in applied magnetic fields up to 62 kOe in a variable temperature cryostat operating between $4^{\circ}K$ to $80^{\circ}K$. Mössbauer spectra have been taken at several values of applied magnetic field at $4.2^{\circ}K$ thus far. Due to the admixture of quadrupole and magnetic splitting, the spectra are complex, and a computer analysis is presently being developed.

The Zn/Fe alloy system has previously been suggested on theoretical grounds as an example of a non-magnetic system which is undergoing spin-fluctuations.

Measurements have also commenced on the Mo/Nb/Fe alloy systems. Several different composition Mo/Nb alloys have been doped with Fe impurities. Since Fe has a well developed local moment in Mo and none in Nb, these alloys offer the possibility of following the development of local moment behavior. Measurements made thus far do not seem to corroborate the simple discontinuous model of Jacarrino and Walker in which the presence of a moment depends only on a minimum number of nearest neighbor Mo atoms.

# ELECTROMIGRATION AND SURFACE MOBILITY IN METALS

Senior Investigator:      H. B. Huntington

This project became operational in June of this year with appointment of a postdoctoral associate to work on the above topic. The research is theoretical and has as its long-term objective a better understanding of electromigration as it affects the thin metal films used in integrated circuitry. As the mass transfer in such films is clearly not a bulk transport, interest is attracted to surface and grain boundary migration. A start will be made with the consideration of the atomic motions at the free surface. The electron distributions at flat and serrated surfaces is being developed according to some simple models and the influence of these electron-ion binding on "ad-atom" motion will be explored.

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    Film Microanalysis"
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    "A Pressure Induced Disappearance of the $\gamma_2$ ($HgSn_{7-8}$) Phase in
    Dental Amalgam"
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    "Microphase Separation in Mixtures of Block Copolymers With the
    Corresponding Homopolymers: Zeroth Approximation"
        Presented at the Chicago Meeting of the American Chemical Society

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    "The Effects of Particles on Fracture Processes in Magnesium Alloys"
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        No. 4 (April 1970)

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